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# Hydrated Minerals on Asteroids: The Astronomical Record

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## 1 Abstract

Knowledge of the hydrated mineral inventory on the asteroids is important for deducing the origin of Earth's water, interpreting the meteorite record, and unraveling the processes occurring during the earliest times in solar system history. Reflectance spectroscopy shows absorption features in both the 0.6–0.8 and 2.5–3.5  $\mu\text{m}$  regions, which are diagnostic of or associated with hydrated minerals. Observations in those regions show that hydrated minerals are common in the mid-asteroid belt, and can be found in unexpected spectral groupings, as well. Asteroid groups formerly associated with mineralogies assumed to have high temperature formation, such as M- and E-class asteroids, have been observed to have hydration features in their reflectance spectra. Some asteroids have apparently been heated to several hundred degrees Celsius, enough to destroy some fraction of their phyllosilicates. Others have rotational variation suggesting that heating was uneven. We summarize this work, and present the astronomical evidence for water- and hydroxyl-bearing minerals on asteroids.

## 2 Introduction

Extraterrestrial water and water-bearing minerals are of great importance both for understanding the formation and evolution of the solar system and for supporting future human activities in space. The presence of water is thought to be one of the necessary conditions for the formation of life as

we know it. Furthermore, the long-term survival of human-staffed bases on other planets is critically dependent upon the existence and exploitation of an easily-reached water source. Current theories for the origin of Earth's ocean require a contribution from both asteroids and comets, although the relative importances of the asteroidal and cometary fractions is still under investigation (Delsemme, 2000; Morbidelli *et al.*, 2000). Asteroids are the primary source of meteorites, many of which show evidence of an early heating episode and varying degrees of aqueous alteration (*e.g.* DuFresne and Anders, 1962). The identification and characterization of hydrated minerals (defined in this chapter as any mineral containing H<sub>2</sub>O or OH) among the asteroids is important for understanding a wide range of solar system formation and evolution processes.

## 2.1 Water in the Solar Nebula and Solar System

Because oxygen is the third most abundant element in the solar system (after hydrogen and helium), its stable hydrogen compound is expected to be common. Indeed, water is found throughout the outer solar system on satellites (Clark and Mc Cord, 1980; Clark *et al.*, 1984), Kuiper Belt Objects (KBOs) (Brown *et al.*, 1997), and comets (Bregman *et al.*, 1988; Brooke *et al.*, 1989) as ice, and on the planets as vapor (Larson *et al.*, 1975; Encrenaz *et al.*, 1999). It is also found bound into minerals (as well as at the polar caps) on Mars (Sinton, 1967; Blaney, 1991; Bell and Crisp, 1991), Europa (McCord *et al.*, 1999), and some asteroids (Lebofsky, 1978; Feierberg *et al.*,

1981), and of course as vapor, liquid, ice, and bound into minerals here on Earth.

The heliocentric distance at which the temperature in the solar nebula allowed water ice to condense is sometimes called the “snow line” (or “ice line” or “dew line”). This distance falls within the current asteroid belt, though the exact distance depends upon the specific model parameters used and the nebular age considered (Cyr, 1998). Once condensed, ice grains may then have migrated inward toward the Sun through gas drag (Cyr *et al.*, 1998). This would potentially allow water to be available for accretion into planetesimals located throughout much of the asteroid belt, even if the snow line were relatively distant.

Current hypotheses postulate asteroids began as mixtures of water ice and anhydrous silicates. A heating event early in solar system history was responsible for creating magma on some bodies (like 4 Vesta), and melting the ice and driving aqueous alteration on others (such as 1 Ceres and 2 Pallas), but apparently was too weak to do either in some cases (*e.g.* Trojan asteroids). Both electrical induction heating caused by a solar-wind plasma flow and heating by  $^{26}\text{Al}$  decay have been postulated as the mechanisms that generated the high temperatures which caused the probable differentiation of some of the asteroids (Herbert and Sonett, 1979; Grimm and McSween, 1993) which produced the iron meteorites. For the carbonaceous chondrites, the heating event was apparently sufficient to melt the internal

ice and drive aqueous alteration reactions, creating hydrated minerals. For most carbonaceous chondrites, the heating did not pass the point where hydrated minerals would begin to dehydrate, though the CV meteorites show evidence of dehydration (Krot *et al.*, 1997).

## 2.2 Hydrated Minerals

Hydrated minerals include both silicates and non-silicates in the scope of this review. Phyllosilicates (or “clay minerals”) are commonly found on Earth as weathering products of rocks or in hydrothermal systems. Non-silicate hydrated minerals include such species as the oxides brucite and goethite, the carbonate hydromagnesite, and the sulfide tochilinite, each of which is known in the meteorite collection (Rubin, 1996). Although a full discussion of the petrogenesis and classification of hydrated minerals is beyond the scope of this paper, we note that formation of hydrated minerals, particularly clay minerals, occurs rapidly and easily in environments where anhydrous rock and water are together. Serpentine-group, smectite-group, and chlorite-group minerals are the phyllosilicates most common in meteorites (Rubin, 1996), as detailed in Section 3. The different clay groups have different numbers of OH groups between the two SiO<sub>2</sub> layers. In some cases in addition to the structural OH, water molecules are adsorbed between the silicate layers. Depending on the cations involved, the layers can range from being only weakly held together by the water molecules, or strongly held by shared oxygen atoms. Phyllosilicates range from serpentine with 2 OH

groups for each silicon to clays such as talc which have one OH for each silicon. Micas have 2 OH groups for each 3 silicon atoms, but are not generally seen in meteorites. Deer *et al.* (1971) give complete compositional and structural details of these minerals.

Studies of hydrated minerals on asteroids are important both for what they tell us about the specific body under study and for insights into the population as a whole. The suite of hydrated minerals present on an asteroid provides clues as to which meteorite groups are appropriate analogs. The distribution of hydrated minerals in the asteroid belt touches upon questions of the homogeneity of the solar nebula, the heat sources present, and how much mixing of planetesimals occurred. Because absorption features from hydrated minerals are often the only ones present in reflectance spectra of low-albedo asteroids, they provide one of the only means of determining compositions for these bodies by remote sensing.

Knowledge of the presence or absence of hydrated minerals is also critical to the interpretation of asteroid densities. The most important factors in meteorite densities are the amount of metal and the amount of hydrated minerals (Consolmagno, this volume). The meteorites with the lowest densities are pervasively aqueously altered, like Tagish Lake and Orgueil. Knowledge of the hydration state of an asteroid, therefore, can be used for inferring its porosity and internal structure.

Hydrated minerals give rise to absorption features throughout the visible

and near-infrared, as reviewed in Gaffey *et al.* (1993b). However, many of these features are not observable using remote sensing techniques because of telluric spectral absorption bands (detailed below). Two spectral regions have been the focus for hydrated mineral studies on asteroids: the 3- $\mu\text{m}$  region spanning 2.4–3.6  $\mu\text{m}$ , and the visible between 0.4–0.9  $\mu\text{m}$ . Since the publication of Asteroids II, much fruitful work has been done in the former region, and study of the latter region for hydrated minerals has grown from practically nil. The highlights of research in each area are detailed below. Section 3 touches upon the hydrated minerals present in the meteorite collection, current theories about their creation, and spectral studies of hydrated minerals in meteorites. Astronomical observations, including possible complexities in data collection and analysis and the techniques used to counter these complexities, appear in Section 4. Interpretations of the astronomical observations, separated by spectral classes, make up Section 5. Section 6 discusses the correlations found between the visible and infrared observations of hydrated minerals on asteroids, as well as issues of rotational variability and possible size effects. Section 7 concerns alternatives to hydrated minerals that have been proposed as explanations for the 3- $\mu\text{m}$  absorption band. Future work and open questions are discussed in Section 8. Finally, the major conclusions we can draw about asteroids from observations of hydrated minerals are presented in Section 9.

### 3 Hydrated Minerals in Meteorites

#### 3.1 Provenance of Hydrated Minerals in Meteorites

In the meteorite collection, hydrated minerals are found mostly among the carbonaceous chondrites of metamorphic grades 1 and 2, associated with the CI, CM, and CR carbonaceous chondrite types. These meteorites have mineralogies indicating low levels of metamorphism ( $< 1200$  °C), and evidence for aqueous alteration (Sears and Dodd, 1988; Rubin, 1996). The CI, CM and CR chondrites also are distinct from other chondrites in their oxygen isotope signatures, and oxidation state, which is related to the formation of hydrated minerals during aqueous alteration. The CM and CI carbonaceous chondrites typically contain 5-15%  $H_2O/OH$  by weight, some more than 20% (Salisbury *et al.*, 1991a; Takaoka *et al.*, 2001, Burbine *et al.* this volume).

The CI chondrites are composed almost entirely ( $\geq 90$  vol%) of fine-grained phyllosilicates, including serpentines, though other hydrous and hydroxylated minerals are also present (Browning *et al.*, 1996). The CM chondrites also contain abundant phyllosilicates and other hydroxylated minerals including saponite, talc, and the sulfide tochilinite. The CR chondrites also contain matrix phyllosilicates in the form of Fe-rich serpentine-group minerals, saponite, and chlorite-group minerals (with Ca-carbonates and magnetite associated with the phyllosilicates) (Rubin, 1996). There is evidence of aqueous alteration and some subsequent dehydration in the CV

chondrites (Krot *et al.*, 1997). Although not normally considered hydrated, some ordinary chondrites also have phyllosilicates (like the LL chondrite Semarkona), or show evidence of aqueous processes (the H chondrites Zag and Monahans) (Hutchison *et al.*, 1987; Zolensky *et al.*, 2000). To date, no evidence of hydrated minerals has been found in achondrites.

### 3.2 Nebula, Parent-Body, or Preaccretional?

Thermodynamical arguments suggest that phyllosilicates could not have been formed in the solar nebula since the kinetics of the formation reaction are too slow (Prinn and Fegley, 1989). This has been challenged by Bose (1993), who found that the activation energy used by Prinn and Fegley is too large by a factor of two, and that the timescale using the correct activation energy is well within the lifetime of the solar nebula. Recent work by Rietmeijer and Nuth III (2000) shows that gas-to-solid condensation in the MgO-FeO/Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system results in Si-rich saponite dehydroxylates, which are metastable. They propose that in the solar nebula dust grains of this composition would be formed and be highly reactive during both dry thermal and aqueous alteration, ensuring that they would eventually be altered.

There is some observational evidence that silicate dust found in rims around grains was hydrated before it was incorporated into the carbonaceous chondrites (Metzler *et al.*, 1992). However, textural evidence from these meteorites shows that the majority of the hydrated minerals formed

on parent bodies in the presence of liquid water. It is still uncertain whether those parent bodies were the size of the asteroids we see today or were still accreting into larger bodies (*e.g.* Bischoff, 1998). A more thorough discussion of aqueous alteration processes on asteroids as understood through meteorite studies is provided in Zolensky and McSween Jr. (1988) and current research topics can be found in Zolensky *et al.* (1997).

### 3.3 Fluid Inclusions

Hydrated minerals are most abundant on CI and CM carbonaceous chondrites, but occur to a lesser extent in other chondrites as well. Recently, fluid inclusions have been discovered in Monahans and Zag, both H ordinary chondrites (Zolensky *et al.*, 1999; Zolensky *et al.*, 2000). Early analysis shows that the fluid is a brine, and has prompted a search for fluid inclusions on other meteorites that could have been overlooked. Saylor *et al.* (2001) searched 19 carbonaceous chondrites, and find fluid inclusions on 5, with possible inclusions on several others. The three CM2 meteorites with inclusions were moderately to highly aqueously altered. Meteorites both more and less aqueously altered were not found to have inclusions, which may mean that a narrow range of conditions are necessary for fluid inclusions to form and be retained. Although this finding is of tremendous importance for analysis of direct samples of asteroidal water, fluid inclusions are not likely to be detected by remote sensing. The 3- $\mu\text{m}$  band detected by remote sensing arises only from (at most) the outer few tens of microns of the sur-

face material, where the presence of fluid inclusions is unlikely, and only a minor contribution at best compared to the presence of phyllosilicates in the regolith.

### 3.4 Meteorite Spectroscopy in the 3- $\mu$ m Region

Meteorites have come under increasing scrutiny in the 3- $\mu$ m spectral region in the last decade. Salisbury *et al.* (1991a) devised an empirical relation between the adsorbed/telluric-derived water content of (nominally anhydrous) minerals and their band depth in the 3- $\mu$ m region, as measured in air. Miyamoto and Zolensky (1994) used spectra of heated samples of powdered carbonaceous chondrites, and showed that the integrated intensity of the 3- $\mu$ m band (found by numerically integrating the area of the absorption feature in a continuum-removed reflectance spectrum) was closely correlated to the observed hydrogen content of carbonaceous chondrites. Sato *et al.* (1997), in turn, correlated the reflectances at 2.90 and 3.20  $\mu$ m divided by the reflectance at 2.53  $\mu$ m to the integrated intensity. This set of empirical relations allows the hydrogen/silicon ratio to be determined for remote asteroid observations, assuming the meteorite powders studied by Miyamoto and Zolensky and Sato *et al.* are similar to asteroid regoliths. The H/Si ratio for 433 Eros was determined in this way by Rivkin and Clark (2001), who found an upper limit of 3% H<sub>2</sub>O for that body. Caution should be taken, however, as the integrated intensities of the same meteorite can have a relatively large scatter (Rivkin, 1997).

Calvin and King (1997) measured the spectra of Fe-bearing phyllosilicates including serpentines and berthierines, and showed that simple linear combinations of Fe- and Mg-phyllosilicates closely approximate the spectra of CM and CI chondrites, in particular the shape of the 3- $\mu\text{m}$  band.

Most asteroids have shallower band depths than the common hydrated meteorites. Hiroi *et al.* (1996) found that the best matches to the spectra of large C-class asteroids in the 3- $\mu\text{m}$  region were unusual thermally metamorphosed CI/CM chondrites. This has been interpreted as evidence for heating events on the largest C asteroids, like 1 Ceres and 2 Pallas, with peak temperatures up to 500-600 °C, as detailed further in Section 6. This work assumes that “space weathering” effects in the 3- $\mu\text{m}$  region and/or on low-albedo asteroids are negligible. However, as mentioned in Section 8.2 (and in further detail in the chapter by Clark *et al.*), the effect of “space weathering” on low-albedo objects is currently an open question.

## 4 Astronomical Observations

### 4.1 Infrared Wavelength Observations

Water and hydroxyl-bearing minerals give rise to diagnostic absorptions throughout the infrared. A 3- $\mu\text{m}$  absorption feature is typically caused by a combination of the very strong OH-radical absorption feature and the very strong first overtone of the 6- $\mu\text{m}$  H<sub>2</sub>O fundamental. Adsorbed water has a symmetric stretch mode giving rise to an absorption feature at 3.1  $\mu\text{m}$

and an anti-symmetric stretch feature at  $2.9 \mu\text{m}$ . Structural hydroxyl (OH) that has been incorporated into mineral lattices produces a stretch absorption at  $2.7 \mu\text{m}$ . The depth of the fundamental  $\text{H}_2\text{O}/\text{OH}$  feature depends on many parameters besides abundance of hydrated material, including particle size, albedo, and temperature. However, water abundances as low as fractions of a weight percent are observable using  $3\text{-}\mu\text{m}$  spectroscopy (Salisbury *et al.*, 1991a). Laboratory studies have shown that higher order overtones at shorter wavelengths ( $1.4$  and  $1.9 \mu\text{m}$ ) are masked more easily by opaque minerals than the  $3\text{-}\mu\text{m}$  feature (Clark, 1981), and they are not always seen even in freshly-fallen, phyllosilicate-bearing meteorites (Hiroi *et al.*, 2001a). In addition, observations of these overtone bands on asteroids may be difficult or impossible even in high-albedo mineral assemblages; reflectance spectra of Mars analogs containing hydrated minerals shows that the  $1.9 \mu\text{m}$  band greatly decreases in strength as the atmospheric pressure decreases, suggesting it will not be observed on the atmosphereless asteroids (Bishop and Pieters, 1995).

The  $3\text{-}\mu\text{m}$  absorption feature in minerals is shifted in wavelength relative to the telluric absorption (see Figure 1), and is much broader than the atmospheric band, though the center of the OH band at  $2.7 \mu\text{m}$  is not observable from the Earth.

At wavelengths near  $3 \mu\text{m}$ , thermal flux from objects in the asteroid belt can become a significant fraction of the total flux and must be modeled and

removed to give a true idea of the reflectance spectrum. The specifics of how much thermal flux is emitted depends critically on variables such as solar distance at the time of observation as well as fixed values such as diameter and albedo, however for most main-belt low-albedo asteroids the thermal contribution is 1–10% of the total flux at 3.1–3.5  $\mu\text{m}$ . A “Standard Thermal Model” (STM) for asteroids was formulated by Lebofsky *et al.* (1986) for use with 3- $\mu\text{m}$  observations. Thermophysical models including values for thermal inertia and rotation rate have been developed as well as refinements to the STM for near-Earth asteroids. Although a thorough review of asteroid thermal models is beyond the scope of this chapter, Lebofsky and Spencer (1989) gives a review of the state of the field as of 1989, and the chapter by Harris *et al.* in this book updates advancements since that time. Because the uncertainty in the thermal contribution is typically much smaller than the observational uncertainties at  $\sim 2.95 \mu\text{m}$ , where band depths are typically calculated, the uncertainties in the thermal flux are typically neglected in band depth measurements. The thermal models do affect band shape beyond  $\sim 3.1 \mu\text{m}$ , and typically the preferred thermal model is one which gives a continuum slope at the long-wavelength end of the 3- $\mu\text{m}$  band consistent with the continuum slope shortward of 2.5  $\mu\text{m}$ .

There are other species that can give rise to absorption features near 3  $\mu\text{m}$ , but all are ices that are not stable on asteroidal surfaces (carbon dioxide, methane, ammonia). The  $\text{NH}_3^+$  ion gives rise to a shallow feature

near  $3.07 \mu\text{m}$ , and has been reported in an ammoniated phyllosilicate on Ceres by King *et al.* (1992), as detailed below. Macromolecular organic solids have absorption features near  $3.4 \mu\text{m}$ . Although fully expected on outer-belt asteroidal surfaces, no confirmed organic feature has yet been seen (Dumas *et al.*, 1998), though methanol or a product of methanol has been found in the spectrum of the Centaur 5145 Pholus (Cruikshank *et al.*, 1998). A search for an overtone of CN-bearing organic material at  $2.1\text{--}2.4 \mu\text{m}$  on outer-belt asteroids yielded no detections (Howell, 1995). An absorption feature due to an Al-OH stretch near  $2.2\text{--}2.3 \mu\text{m}$  commonly seen in terrestrial clays has not to date been seen in asteroids or meteorites.

#### 4.2 Visible Wavelength Observations

Spectra of main-belt C- and G-class asteroids and some C-, G-, and P-class asteroids in the Cybeles (mean semi-major axis  $a \sim 3.4$  AU) show an absorption feature centered near  $0.7 \mu\text{m}$  with a width of roughly  $0.25 \mu\text{m}$ , attributed to an  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge transfer transition in oxidized iron found in phyllosilicates (Vilas and Gaffey, 1989). Figure 5 contains examples of this feature. Independent research by Sawyer (1991) showed that this feature is very common among the main-belt low-albedo asteroids. This absorption feature and absorption features seen in the laboratory spectra of CM2 carbonaceous chondrite meteorites and terrestrial phyllosilicates are similar in band position and strength, further supporting the connection between the C-class asteroids and carbonaceous chondritic material formed

through the aqueous alteration process. King and Clark (1997) caution that a feature near  $0.7 \mu\text{m}$  is found in many different minerals, and that its presence alone is not diagnostic for phyllosilicates. The vast majority of minerals with a  $0.7\text{-}\mu\text{m}$  band are Fe and OH-bearing silicates, however. As detailed in Section 6, joint studies at both  $0.7$  and  $3 \mu\text{m}$  show that in low-albedo asteroids (the C, B, G, F, and P classes) at least, the correlation between these features is quite good. Since CCD visible spectra are relatively easy to obtain with moderate sized telescopes, many efforts have been made to observe this feature, and determine the hydration state of asteroids (Barucci *et al.*, 1994; Fitzsimmons *et al.*, 1994; Barucci *et al.*, 1998; Dahlgren and Lagerkvist, 1995; Dahlgren *et al.*, 1997; Lazzarin *et al.*, 1995; Carvano *et al.*, 2001; Jewitt and Luu, 1990). Fornasier *et al.* (1999) found 65% of the mostly C-class objects they observed to have the  $0.7\text{-}\mu\text{m}$  feature, in good agreement with the fraction of C asteroids with the  $3\text{-}\mu\text{m}$  feature (Table 2). It is unclear at this time why later visible surveys (as well as the  $3\text{-}\mu\text{m}$  surveys) disagree with the quoted results of Sawyer (1991).

Thirteen C-, P-, and G-class (and 1 K-class) asteroids observed in the UV/blue spectral region show an absorption feature at  $0.43 \mu\text{m}$  attributed to an  $\text{Fe}^{3+}$  spin-forbidden transition in iron alteration minerals similar to jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) (Vilas *et al.*, 1993; Cochran and Vilas, 1997). A strong correlation between the  $0.43\text{-}\mu\text{m}$  feature and the  $0.7\text{-}\mu\text{m}$  feature was apparent in these asteroids, although none of the asteroids was observed

in the UV spectral region on more than one night in the original 1993 work. The feature is commonly found in the C and G classes, and absent in the D class, in agreement with results from the 3- $\mu\text{m}$  region (Jarvis, personal communication). Because of interference by nearby absorption lines in solar-analog standard stars, however, full use and exploration of this absorption feature has been problematic (Jarvis *et al.*, 1998).

Spectra of 5 low-albedo F-, C-, P- and D-class asteroids show weak absorption features centered near 0.60–0.65  $\mu\text{m}$  and near 0.8–0.9  $\mu\text{m}$  (Vilas *et al.*, 1994). These features have been tentatively identified as due to ferric iron absorptions in iron alteration minerals such as the oxyhydroxide goethite ( $\alpha\text{-Fe}_3^+\text{O(OH)}$ ), iron oxide hematite ( $\text{Fe}_2\text{O}_3$ ), or iron sulfate jarosite, although none of these minerals has been identified in the terrestrial meteorite collection. Spectra of low-albedo asteroids showing the 0.7- $\mu\text{m}$  feature sometimes also have smaller absorption features near 0.6 and 0.9  $\mu\text{m}$  superimposed on the 0.7- $\mu\text{m}$  feature (Vilas *et al.*, 1994). The possibility that these features are the iron alteration features seen in conjunction with the phyllosilicate absorption was proposed (Vilas *et al.*, 1994), but spinel-group minerals are also a possibility (Hiroi and Vilas, 1996). The presence and interpretation of these features remain open questions pending future work with extended wavelength coverage to the near-IR, and perhaps a dedicated survey.

Table 1 lists the absorption features associated with hydrated minerals

that have been identified to date in the spectra of asteroids and their current mineralogical interpretations. In the visible/near infrared spectral region (0.3–2.5  $\mu\text{m}$ ), these are weak absorption features having typical depths of 1–5% of the background continuum. The 3- $\mu\text{m}$  feature typically has a depth of 15–30% or more in low-albedo asteroids. The widest features ( $> 0.3 \mu\text{m}$ ) can be detected at smaller depths, but care must be taken in determination of the continuum. The 3  $\mu\text{m}$  feature often extends to 4  $\mu\text{m}$  in laboratory spectra, but due to the uncertainty in the thermal emission in the case of asteroids closer to the sun than 3 AU, the band continuum is usually measured between 2.5 – 3.35 (or 3.5)  $\mu\text{m}$ . The band depth is measured at 2.95  $\mu\text{m}$  relative to this continuum.

## 5 Results for Asteroid Classes

The hydrated mineral features on asteroids appear to have one of two general band shapes, corresponding roughly to the rounded H<sub>2</sub>O-like absorption feature, and the “checkmark” OH-like absorption feature (see Figure 2). In general (and as detailed below), hydrated minerals on low-albedo asteroids tend to have the checkmark shape, while on high-albedo asteroids they have a rounded shape, when band shapes can be determined.

Table 2 summarizes the results for the major asteroid classes. As can be seen, there are large differences in the fraction of hydrated members from class to class. The specifics for each class will be discussed below. We note,

Wavelength ( $\mu\text{m}$ )	Width ( $\mu\text{m}$ )	Transition	Reference
<0.4	>0.1	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ intervalence charge transfer transition	e.g. Gaffey and McCord (1979)
0.43	0.02	$6A1 \rightarrow 4A1,4E(G)$ $\text{Fe}^{3+}$ spin-forbidden as in jarosite	Vilas et al. (1993a)
0.60 - 0.65	0.12	$6A1 \rightarrow 4T2(G)$ $\text{Fe}^{3+}$ in iron alteration minerals	Vilas et al. (1994a)
0.7	0.3	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ in phyllosilicates	Vilas and Gaffey (1989)
0.80 - 0.90	0.08	$6A1 \rightarrow 4T1(G)$ $\text{Fe}^{3+}$ in iron alteration minerals	Vilas et al. (1994a)
3.0	>0.7	structural hydroxyl (OH) interlayer and adsorbed H <sub>2</sub> O	Lebofsky (1978,1980)
3.07	0.2	H <sub>2</sub> O ice NH <sub>4</sub> -bearing saponite	Lebofsky et al. (1981) King et al. (1992)

Table 1: Observed Absorption Features Associated with Hydrated Minerals on Asteroids

however, that because of the possibility of surface variegation (discussed further in Section 6), the number of hydrated asteroids should be considered a lower limit. Because the Tholen asteroid taxonomy (Tholen and Barucci, 1989) was the most widely used one during the period in which this work has been done, we will use the Tholen taxonomy in most cases below. We note that interpretations of asteroid populations are necessarily influenced by the choice of classification schemes, and that labeling a potentially diverse group of mineralogies with a similarly diverse set of formation conditions with a single letter should be undertaken with care.

## **5.1 Low-Albedo Objects**

### **5.1.1 C-class and related asteroids**

Jones *et al.* (1990) observed 19 low-albedo objects, mostly of the C class and sub-classes. They determined that the fraction of hydrated asteroids decreased with increasing semi-major axis from the middle of the asteroid belt outwards. This was interpreted as evidence that the asteroids were originally composed of mixtures of ice and anhydrous silicates, and that hydrated minerals were formed through an aqueous alteration event rather than in the nebula. In this interpretation, the mid-belt hydrated asteroids were heated enough to melt the internal ice and form phyllosilicates while the outer belt objects never achieved a temperature high enough to melt ice. This paradigm has continued to this day.

The C, B, G, and F asteroids have been proposed as comprising an alter-

Tholen Class	3 $\mu\text{m}$			0.7 $\mu\text{m}$		
	Observed	With Band*	Pct.	Observed	With Band	Pct.
C	32	20	63%	45	20	44%
B	1	1	100	1	0	0
G	5	5	100	6	6	100
F	5	1	20	5	2	40
T	4	3	75	5	0	0
D/P	20	3	15	22	4	18
K/L	5	2	40	1	0	0
S	24	1	4	4	0	0
E	6	4	67	1	0	0
M/W	27	10	37	23	1	4

Table 2: Asteroids observed at 3  $\mu\text{m}$  and at 0.7  $\mu\text{m}$ , with the fraction showing absorption features for each wavelength region. \* The uncertainties vary, so the band depth limits are not uniform in these data. At both wavelengths, variability in this feature might be present on some asteroids, so the number and percentage showing the absorption feature is a lower limit. Note that the B asteroid is 2 Pallas, which may not be representative of the B class as a whole. This table includes data from Lebofsky (1980), Feierberg et al. (1985), Jones et al. (1990), Rivkin et al. (1995), Howell (1995), Rivkin (1997), Merényi et al (1997) , Jarvis et al (1999) as well as further unpublished data from Rivkin and Howell. For those asteroids with multiple designations (*e.g.* CF, XC), the first letter was taken as the class. The K and L classes are from Bus (1999), the W class from Rivkin et al. (1995)

ation sequence (Bell *et al.*, 1989 and references therein). These sub-classes all have different fractions of hydrated members, from the ubiquitously-hydrated G asteroids (all six observed have a feature) to the mostly anhydrous F asteroids (one of five hydrated). This supports the idea of an alteration sequence, where the G asteroids were heated to the point where melted ice could cause pervasive aqueous alteration, and the F asteroids were heated further to the point that the hydrated minerals were destroyed. However, Sawyer (1991) interprets the F asteroids as unaltered rather than heated and dehydrated, since dehydration and recrystallization would be expected to raise the albedos of F asteroids beyond the observed values. The unaltered interpretation of Sawyer assumes an electromagnetic-induction heating scenario, with the exteriors of the parent bodies heated more than the interiors. With the relatively small sample size of F asteroids, the interpretation of F asteroids remains unsettled though their association with C asteroids seems secure.

The largest asteroid, 1 Ceres was observed by Lebofsky *et al.* (1981) to have an absorption feature at  $3.07 \mu\text{m}$  within the broad hydrated mineral feature. This was interpreted as water ice, which was shown to be marginally stable near Ceres' poles (Lebofsky *et al.*, 1981). Later work by King *et al.* (1992) suggested that this sub-feature was due to  $\text{NH}_3^+$ -bearing phyllosilicates. Rivkin (1997), using a combination of first-look ISO data and UKIRT observations, found ammoniated smectite to be a good fit for the spectrum of

Ceres in the 2.4–2.6  $\mu\text{m}$  region, including the 2.6–2.8  $\mu\text{m}$  area observed from ISO and unobservable from the ground (Figure 3). Ammonium phyllosilicates are relatively rare on Earth, found in hydrothermal deposits. Lewis and Prinn (1984) considered the possibility of  $\text{NH}_3^+$ -rich brines on asteroids, which could be the origin of these minerals on Ceres. However, observations of OH near the sunlit pole of Ceres by (A'Hearn and Feldman, 1992) are more consistent with the presence of water ice. The discovery of a Ceres-like band shape on 375 Ursula suggests that the mineralogy may not be unique to Ceres (Rivkin et al., in preparation).

In general, most low-albedo asteroids with absorption features have band shapes indicative of OH-dominated minerals rather than  $\text{H}_2\text{O}$ -dominated ones, seen for example in Figure 4, a fit to the spectrum of 13 Egeria from Rivkin (1997). Both types of minerals have been seen in meteorites. The explanation for this may be that the  $\text{H}_2\text{O}$  in these minerals may be unstable in the vacuum of space while the structural OH can remain; but then why do the higher-albedo objects show a  $\text{H}_2\text{O}$ -like feature? Another possibility is that the water-rich meteorites may come from a relatively restricted area on its parent body.

The 3- $\mu\text{m}$  band depths for C-class asteroids are not as deep as those found in the laboratory for their putative analogs, the hydrated carbonaceous chondrite meteorites. In some cases, band depths are less by a factor of three or more. Differences in determining the continuum, and choosing

where to measure the band depth may account for some of the discrepancy, though real differences are also present in some cases. One explanation that has been suggested for this is that the asteroids have experienced some degree of thermal processing, driving off water and destroying hydrated minerals (Hiroi *et al.*, 1996). Another possibility is that “space weathering” processes similar to those found at shorter wavelengths could be at work (Clark *et al.* this volume). How micrometeorite impacts might affect the hydrated mineral inventory of an aqueously altered body will no doubt be the subject of future work. We may speculate that the energy of impact might go to liberating water before it can create the nanophase iron seen in lunar soils and believed to be present on chondritic, anhydrous surfaces (Noble *et al.*, 2001; Sasaki *et al.*, 2001). As a result, the reddening and darkening effects seen on lunar surfaces and laboratory simulations might not occur on hydrated bodies until they are dehydrated (which might never happen). Alternately, we note that “space weathering” effects due to nanophase iron coatings are not currently expected to be very important on low-albedo objects like the C-class asteroids (Pieters *et al.*, 2000). This is because they are most effective when coating transparent minerals like olivine and pyroxene; while nanophase iron has a lower albedo than olivine and pyroxene and small amounts can radically change a spectrum, it has a higher albedo than the opaque minerals present in the C, P, D, etc. asteroids and will have little effect. A final possibility is that the meteorites we have collected are from

a small subset of the C-class (and related) asteroids, and the differences in spectra that we see should be taken at face value. Burbine (1998) proposed that the G-class asteroids could contain the parent bodies of the CM meteorites. Interestingly, these asteroids have the deepest 3- $\mu\text{m}$  bands, and Rivkin and Davies (2002) have calculated that the G-class asteroids 13 Egeria and 106 Dione, as well as the CU-class asteroid 51 Nemausa, have water contents consistent with the average CM chondrite values, which range from 6.5–12% (Jarosewich, 1990).

Hydrated minerals and internal water ice have been invoked as a means to account for the lower-than-expected densities of asteroids (Veveřka *et al.*, 1997; Merline *et al.*, 2000) and the martian satellites (Avanesov *et al.*, 1991). However, the lack of a 3- $\mu\text{m}$  absorption feature on 253 Mathilde does not support abundant internal ice or hydrated minerals on that body (Rivkin *et al.*, 1997a), suggesting porosity is the sole cause of its low density. Similarly, the lack of absorption features on Phobos and Deimos (Murchie and Erard, 1996; Rivkin *et al.*, 2002) suggests that porosity is the main cause of their low densities. This topic is covered in more detail in Britt *et al.* in this volume.

### 5.1.2 D/P-class Asteroids

The D-class and P-class asteroids dominate the outer belt and Trojan clouds. Observations in the 3- $\mu\text{m}$  region by (Jones *et al.*, 1990), Lebofsky *et al.* (1990), and Howell (1995) found no hydrated asteroids of these classes be-

yond 2.9 AU. Asteroid 336 Lacadiera, interestingly, shows evidence of variation in its 3- $\mu\text{m}$  band (Howell, 1995), and is the D-class asteroid with the smallest semi-major axis in the main-belt by far (2.25 AU). Asteroid 50 Virginia, classed X by Tholen, was found to have an albedo of 0.05, based on combined visible and thermal infrared observations, and is thus a P asteroid. A 3  $\mu\text{m}$  band was seen on Virginia, making it the only hydrated P asteroid known. Its semi-major axis is 2.65 AU, again much closer than most P-class asteroids. In the Bus taxonomy, 336 Lacadiera is Xk, and 50 Virginia is Ch, suggesting they are distinct from the outer-belt P and D asteroids. Further work by Emery and Brown (2001) also found no 3- $\mu\text{m}$  absorptions on Trojan asteroids.

A detailed study of the Trojan asteroid 624 Hektor by Cruikshank *et al.* (2001) found no 3- $\mu\text{m}$  feature, but showed that up to 40% serpentine (representing  $\sim$  6% water) could still be present but masked by low-albedo constituents (they use elemental carbon). Therefore, they argue, the Trojan asteroids could have relatively abundant hydrated minerals, contrary to the interpretations of Jones *et al.* (1990). Cruikshank *et al.* further note that the trend of decreasing 3- $\mu\text{m}$  band strength with heliocentric distance could instead be due to increasing abundance of elemental carbon. Both Cruikshank *et al.* and Jones *et al.* interpret the Trojans as potentially ice-rich bodies, with near-surface ice masked by low-albedo constituents and/or devolatilized by impacts.

Studies of the Tagish Lake carbonaceous chondrite show a reflectance spectrum quite close to the D-class asteroids in the 0.3–2.5  $\mu\text{m}$  region, and it has been proposed as an analog for those asteroids (Hiroi *et al.*, 2001b). However, Tagish Lake has a significant absorption feature in the 3- $\mu\text{m}$  region ( $\sim 20\%$ ) which is absent in the D asteroids. Hiroi *et al.* propose that this mismatch may be relatively minor due to large observational uncertainties in the asteroid spectra, and that any mismatches that do exist could be due to dehydration of the D asteroid regoliths through micrometeorite bombardment. This idea is further discussed in Section 8 for asteroids in general. Tagish Lake has a very low albedo ( $\sim 3\%$ ), with 4-5% carbon and a matrix dominated by phyllosilicates (Roots *et al.*, 2000). The model used by Cruikshank *et al.* (2001) for 624 Hektor had 20% amorphous carbon. Perhaps the regolith of Trojan asteroids becomes particularly concentrated in low-albedo constituents. Or, Tagish Lake could be a fragment of an inner-belt D asteroid, for which hydration features have been seen (such as 336 Lacadiera).

## 5.2 Medium- and High-Albedo Objects

### 5.2.1 E-class and M-class (and W-class) Asteroids

Jones *et al.* (1990), in the course of their studies of outer-belt asteroids, discovered 3- $\mu\text{m}$  absorptions on the M-class asteroids 55 Pandora and 92 Undina, which was completely unexpected on bodies presumed to be analogous to iron meteorites. A survey of 27 M-class asteroids by Rivkin *et al.* (1995) and Rivkin *et al.* (2000) confirmed the presence of this feature on ten of

them, including both 92 Undina and 55 Pandora. They separated the hydrated members of this group to form the “W-class”. The 0.7- $\mu\text{m}$  feature correlated with the 3- $\mu\text{m}$  hydration feature (see below) has also been seen on some of these bodies (e.g. 135 Hertha and 201 Penelope— Busarev and Krugly Yu, 1995; Howell *et al.*, 2001a), reinforcing the hydrated mineral interpretation. In general, however, the 0.7- $\mu\text{m}$  feature has not been seen on W-class asteroids.

Rivkin *et al.* found the 3- $\mu\text{m}$  feature to be correlated with size in a sample of 27 M and W asteroids, with the larger bodies (diameter > 65 km) likely to have the feature (75% with the feature) and the smaller bodies unlikely to have it (10% with the feature). On the basis of these observations as well as polarimetric (Belskaya and Lagerkvist, 1996), radar (Ostro *et al.*, 1993; Magri *et al.*, 1999), and meteorite cooling data (Haack *et al.*, 1990), Rivkin *et al.* (2000) argued that many of the M-class asteroids were not in fact analogous to iron meteorites, but the primitive enstatite chondrites. Although enstatite chondrites with hydrated minerals are not currently known in the meteorite collection, there is no cosmochemical objection to their existence.

E asteroids have also been interpreted as igneous objects, akin to the aubrite (enstatite achondrite) meteorites. They dominate the innermost part of the asteroid belt, in the Hungaria region. They are rare in the asteroid belt as a whole. Rivkin *et al.* (1995) and Rivkin (1997) reported

on six E-class asteroids, and found the largest four of them to show an absorption feature at 3  $\mu\text{m}$ . Aqueous alteration scenarios for aubrites are theoretically possible, though they are not seen in the meteorite collection. None of the survey objects were from the Hungaria region, which still may be the source of the aubrite meteorites known on Earth.

As mentioned in Section 7, Cloutis and Burbine (1999) and Fornasier and Lazzarin (2001) suggested that a feature found near 0.5  $\mu\text{m}$  in some E asteroids may be due to troilite or other sulfides, and that the mineral responsible may also be responsible for the 3- $\mu\text{m}$  feature in E-class, and perhaps M-class asteroids. However, the group of asteroids showing the visible absorption include both those with and without a 3- $\mu\text{m}$  feature, and asteroids with the 3- $\mu\text{m}$  feature include those both with and without the visible feature. Therefore, the two absorptions appear uncorrelated with each other in E-class asteroids.

With the deluge of new visible-region data, and taxonomies that show a continuum of spectral types, the notion of hydrated M and E asteroids is somewhat less shocking. The work of Bus (1999) shows asteroids populate the spectral space between the classical C and X classes, and that there are bodies with spectra that are transitional between the two. Using an artificial neural network to classify asteroids based on their 0.3–2.5  $\mu\text{m}$  spectra, Howell *et al.* (1994b) showed that some nominally M-class asteroids had spectra that were actually more similar to those of C asteroids. Similarly, recent

findings suggest that the albedos of common taxonomic types have a much larger range than previously considered, at least among the near-Earth population (Harris, 2001). Given the blurring of taxonomic lines compared to the time of *Asteroids II*, it is perhaps not surprising that hydrated minerals are being found on asteroids previously considered to be devoid of them (the M asteroids, for example). Furthermore, given the evolving understanding of meteorite delivery (Bottke et al., this volume), and the realization that the meteorite collection may be dominated by a relatively small number of parent bodies, the finding that some asteroid mineralogies are not represented as meteorites is not as bothersome as it may have been a decade ago.

### 5.2.2 S-class Asteroids

The S-class asteroids have been the subject of great controversy throughout the decade since *Asteroids II* was published. Given that the two main interpretations of S asteroid mineralogy are either entirely anhydrous (stony-iron/primitive achondrites) or largely anhydrous (ordinary chondrite meteorites), these asteroids have been expected to show no absorption bands due to hydrated minerals. A compilation of the existing S asteroid spectra by Rivkin *et al.* (1997b) found this to be true. Further observations were motivated by the realization that some OC meteorites do have aqueous alteration products, and in an effort to generate longer-wavelength data for use in spectral mixing models. A spectrophotometric survey of 17 S-class as-

teroids at 3  $\mu\text{m}$  was made by Rivkin from 1998-1999. The asteroids surveyed include 7 S(IV) asteroids, which are those that are most closely related to ordinary chondrites based on their 1–2.5  $\mu\text{m}$  spectrum (Gaffey *et al.*, 1993a). Although these data are still undergoing final analysis, preliminary results show that any absorption features have upper limits on band depth of 5-7%.

Eaton *et al.* (1983) studied 11 asteroids from 3–4  $\mu\text{m}$ , of several classes, including 4 S asteroids. Because the spectra do not extend shortward of 2.5  $\mu\text{m}$ , it is difficult to scale these data to existing near-IR data, and these data are not included in Table 2. However, of the S asteroids observed by Eaton *et al.*, only 8 Flora was interpreted as possibly having a 3- $\mu\text{m}$  absorption band.

The S-class asteroid 6 Hebe has been proposed as the parent body of the H chondrite meteorites (Farinella *et al.*, 1993; Migliorini *et al.*, 1997; Gaffey and Gilbert, 1998). A 3- $\mu\text{m}$  absorption feature of  $5\% \pm 2\%$  was discovered on this body by Rivkin *et al.* (2001), with evidence of rotational variation. The discovery of aqueous alteration products in H chondrite meteorites (Zolensky *et al.*, 2000), and their absence in stony-iron meteorites and other achondrites proposed as S asteroid analogs by Bell *et al.* (1989) (among others), makes this absorption feature an indication that at least the last heating event on Hebe did not melt the surface, and that at least one S-class asteroid is more akin to the primitive meteorites than the igneous ones. Observations of Hebe included in Rivkin (1997) were interpreted as

evidence of an anhydrous surface, though these data have somewhat larger uncertainties than the Rivkin *et al.* (2001) observations, and are consistent with them.

The Near-Infrared Mapping Spectrometer on the Galileo spacecraft obtained data in the 3- $\mu\text{m}$  region for 957 Gaspra and 243 Ida (and its satellite Dactyl). These data have not yet been fully analyzed, but preliminary results show no absorption feature (Fanale and Granahan, reported in Chapman, 1996).

### 5.2.3 K and L Asteroids

The K-class asteroids have spectra intermediate between S and C asteroids, and have been proposed as the CV/CO parent bodies (Bell, 1988; Burbine *et al.*, 2001). Most of them are members of the Eos family and may have a common origin in a collisional event. The L class was created by Bus (1999) as similar to K asteroids, with a steeper UV slope. Both hydrated and anhydrous members of the K and L classes have been seen (Rivkin *et al.*, 1998; Rivkin, 1997), supporting the proposed relationship between these bodies and the CV/CO chondrites. The CV/CO chondrites have some hydrated members as well as some which show evidence of dehydration by subsequent heating (Krot *et al.*, 1997; Rubin, 1996).

## 6 Connections between and variability in the 3- $\mu\text{m}$ and 0.7- $\mu\text{m}$ absorptions

### 6.1 Correlation of 0.7- $\mu\text{m}$ and 3- $\mu\text{m}$ Bands

Vilas (1994) found an 80% correlation between the 3  $\mu\text{m}$  band and the 0.7  $\mu\text{m}$  charge transfer band. The sample of objects was relatively small (27), and the observations at the two different wavelengths had been made many years apart in most cases. In a more recent compilation, 34 of 51 asteroids, or 67% observed at both wavelengths had consistent bands (Howell *et al.*, 2001b). Nevertheless, this provides a useful tool for predicting the likelihood of the hydration state. Based on the presence of the 0.7- $\mu\text{m}$  feature, an empirical algorithm for predicting the presence of water of hydration data from the Eight-Color Asteroid Survey (Zellner *et al.*, 1985) was developed and applied to the ECAS photometry of asteroids and outer planet satellites (Vilas, 1994). The percentage of objects in low-albedo, outer main-belt asteroid classes that test positively for water of hydration increases from P  $\rightarrow$  B  $\rightarrow$  C  $\rightarrow$  G class and correlates linearly with the increasing mean albedos of those objects testing positively (Vilas, 1994). This suggests that the aqueous alteration sequence in the solar system ranges from the P-class asteroids, representing the least-altered objects created at temperatures attained at the onset of aqueous alteration, to the G-class asteroids, representing the upper range of the alteration sequence among low-albedo asteroids. Although this scenario is an oversimplification, it provides a framework for

further investigation. The F class asteroids do not as a group seem to be hydrated, based on both visible and 3  $\mu\text{m}$  spectra. The G class asteroids are all hydrated, and have both 3- $\mu\text{m}$  and 0.7- $\mu\text{m}$  bands. If these are the most extensively altered, the 0.7  $\mu\text{m}$  band might be expected to be absent, with all the  $\text{Fe}^{2+}$  having been converted to  $\text{Fe}^{3+}$ .

The M-class asteroids with a 3- $\mu\text{m}$  absorption band do not generally have the 0.7- $\mu\text{m}$  band. Along with the lack of an FeO absorption edge at 0.3  $\mu\text{m}$ , this may be evidence for a different composition for those M class objects with a 3  $\mu\text{m}$  absorption, hence the W class (Rivkin *et al.*, 2000). Alternatively, these objects could represent a mixture of metals with phyllosilicates that have been significantly altered to the extent that  $\text{Fe}^{2+}$  has been leached out of the phyllosilicates and sequestered as  $\text{Fe}^{3+}$  in opaque phases such as magnetite or iron sulfides. This allows the albedo to increase as the particle size of the opaque grains increases reducing the grain surface area that can absorb light, so that light is reflected not absorbed. This process also reduces the presence of oxidized iron, thus removing the 0.7- $\mu\text{m}$  absorption feature (Vilas, 1994).

The inconsistencies in the observations prompted an attempt to examine the relationship between these bands more closely (Howell *et al.*, 2001a). Rotationally resolved visible spectra were obtained of a number of asteroids which did not have concurrent bands at 3  $\mu\text{m}$  and 0.7  $\mu\text{m}$ . Several possibilities could account for these bands not being concurrent: If the hydrated

silicates are unevenly distributed across the asteroid surface, then perhaps rotational variability explains the discrepancy. Only Fe-bearing hydrated silicates exhibit the 0.7- $\mu\text{m}$  band, so the presence of the 3- $\mu\text{m}$  band alone might occur on Fe-poor objects. The 3- $\mu\text{m}$  band is stronger, so it could be detected on some low-albedo objects in cases where the weaker 0.7- $\mu\text{m}$  band cannot be seen. However, the 0.7- $\mu\text{m}$  band should not be present when 3- $\mu\text{m}$  band is absent, unless it can also arise from anhydrous minerals. While some high-albedo salts have a 3- $\mu\text{m}$  feature, the asteroids in the Howell *et al.* study are in taxonomic classes with low albedos, which puts strong constraints on the abundance of these minerals.

## 6.2 Thermal alteration and hydrated minerals

Hydrated silicates can be used as very sensitive tracers of thermal history (Hiroi *et al.*, 1996). In addition to altering olivine and pyroxene to form hydrated silicates (e.g. serpentine), the aqueous alteration process produces oxidized iron which has absorption bands in the visible and UV spectral regions. Moderate subsequent heating can alter the depth or eliminate some or all of these bands. Hiroi *et al.* (1996) finds that Murchison (CM2) material exhibits a strong UV band due to FeO, 0.7- $\mu\text{m}$  band from Fe<sup>2+</sup>-Fe<sup>3+</sup> charge transfer, and 3- $\mu\text{m}$  band due to H<sub>2</sub>O/OH when heated less than 400 °C. Between 400–600 °C, the 0.7- $\mu\text{m}$  band weakens and disappears, and the 3- $\mu\text{m}$  band gets shallower. At temperatures above 600 °C, the 3- $\mu\text{m}$  band disappears as the minerals are completely dehydrated (Figure 6). Asteroid

511 Davida has been observed extensively, and a 3- $\mu\text{m}$  band has been seen with variable depths over at least 25% of the rotation period. However, at a similar sub-Earth latitude, the 0.7- $\mu\text{m}$  band was not seen at any rotation phase. A mild heating episode, occurring after the aqueous alteration, with temperatures reaching 400–600 °C, can explain these observations. Another possibility is that all the  $\text{Fe}^{2+}$  has been converted to  $\text{Fe}^{3+}$ , which would account for the 0.7- $\mu\text{m}$  band being absent on an object where the 3- $\mu\text{m}$  band is seen.

### 6.3 Rotational Variation

Although the visible 0.7- $\mu\text{m}$  band indicates hydration when it is present, when it is not seen no firm conclusions can be drawn about the hydration state. In a sample of 51 asteroids, 31% of those which did not have the 0.7- $\mu\text{m}$  band did have a 3  $\mu\text{m}$  band indicating hydrated minerals (Howell *et al.*, 2001a). Rotational variation is common, and several observations at different rotation phases are necessary to accurately determine if hydrated minerals are present. Examples of rotational variability in 0.7- $\mu\text{m}$  band depth can be seen in Figure 7.

Vilas and Sykes (1996) predict that there should be more surface compositional diversity among smaller-diameter low-albedo asteroids, while the larger-diameter low-albedo asteroids should be individually homogeneous. However, rotationally resolved spectral observations indicate that up to 45% of asteroids have both hydrated and anhydrous surface regions in all size

ranges. Asteroid 10 Hygiea (410 km diameter) has at least 2 distinct surface regions which show the 0.7  $\mu\text{m}$  band, and other distinct regions which show only the 3  $\mu\text{m}$  band. Still other areas have neither band. These observations cannot be explained by the same type of thermal metamorphism described above for 511 Davida, unless material from a wider range of depths is now exposed on the surface of 10 Hygiea. Spectra of asteroid 444 Gyptis (C) on opposite sides of the body show that one side of the asteroid has aqueously altered material, while the other side has no evidence of aqueous alteration products (Thibault *et al.*, 1995).

#### **6.4 Putting it all together in a thermal evolution scenario**

The distribution and diversity of aqueous alteration end products on asteroids in principle tells us about the original composition and the thermal evolution of the asteroids. However, the interaction and interdependence of the many different processes involved make disentangling them a challenge.

Grimm and McSween (1989) propose that radioactive heating is sufficient to aqueously alter asteroid parent bodies, provided that accretion occurs quickly enough. Cohen and Coker (2000) agree that  $^{26}\text{Al}$  can produce sufficient heat for aqueous alteration, if accretion is well underway by 3 Myr after nebula collapse, which agrees with dynamical models (Wetherill, 1990; Weidenschilling and Davis, 2001). While not ruled out, the electrical induction model for heating of asteroids to produce aqueous alteration (Herbert and Sonett, 1979) is no longer strongly supported, based on an improved un-

derstanding of the T-Tauri phase of solar-type stars (Grimm and McSween, 1993). Under both proposed heating mechanisms, most asteroids with diameters above 20 km, between 2.6–3.5 AU (where most of the C-class asteroids are found), would be heated to the point of water mobilization. Larger-diameter asteroids (up to diameters of 100 km) would undergo increasingly greater heating, with the interiors of the asteroids reaching higher temperatures than the surfaces (Herbert and Sonett, 1979; Grimm and McSween, 1993). The formation of Jupiter, however, resulted in asteroid orbits being pumped up in eccentricity and inclination, creating a collisionally disruptive environment (*e.g.*, Davis *et al.*, 1989). Small asteroids observed today are representative of the interiors of larger (but not the largest) asteroids and have likely experienced multiple disruptive events. Asteroids having diameters greater than 100 km would also have been shattered, but remain gravitationally-bound "rubble piles" with material churned by multiple collisions (Davis *et al.*, 1989). The spectral characteristics of the larger-diameter asteroids would represent the combination of thermally-metamorphosed and aqueously-altered material. This scenario predicts the larger asteroids to have more hydrated minerals than the smaller asteroids, since the latter are remnants of heated asteroid interiors, while the surfaces of larger asteroids have always been near the cooler exteriors of their parent bodies. This implicitly assumes similar-sized asteroids had similar starting materials, and thermal, and collisional histories.

The prediction of a size-band depth correlation was tested by applying the results of the algorithm for identifying the 0.7- $\mu\text{m}$  feature (Vilas, 1994) to ECAS photometry of 153 low-albedo asteroids, binned by diameter (Howell *et al.*, 2001a). A trend of fewer low-albedo asteroids having the 0.7- $\mu\text{m}$  feature at smaller sizes is consistent with the hypothesis of Vilas and Sykes (1996) and the scenario outlined above (Table 3).

Diameter range (km)	Number w/0.7- $\mu\text{m}$ feature	Total	Ratio
0 - 50	9	29	0.31
50 - 100	11	40	0.28
100 - 150	32	57	0.56
150 - 200	12	20	0.60
200 - 250	3	7	0.43

Table 3: Percentage of Tholen CBFQ Asteroids Testing Positively for the 0.7- $\mu\text{m}$  Feature Divided by Diameter

However, if both 0.7- $\mu\text{m}$  and 3- $\mu\text{m}$  bands are used, the hydrated fraction is nearly constant with size. The large number of smaller objects observed as part of the SMASS II survey greatly adds to the number of asteroids below 20 km observed spectrally. However, these are observations at a single rotation phase, and should be viewed as a lower limit on the number of objects with hydration on some part of the surface, which is consistent with an *increase* in the hydrated fraction at smaller sizes. Additional study of smaller asteroids is required for a better understanding of how the surface material represents the interior of larger objects, now broken into fragments. A wide diversity seems to exist among asteroids of similar size, which may require a

more complete integration of alteration mechanisms, regolith evolution, and collisional history in order to reach a complete understanding of hydrated surface mineralogy.

## **7 Proposed Alternative Interpretations for Hydrated Mineral Absorption Features**

The interpretation that the 3- $\mu\text{m}$  and 0.7- $\mu\text{m}$  absorption features on asteroids are due to hydrated minerals has been challenged in some quarters. Their presence on the E- and M-class asteroids in particular has led some workers to propose alternative explanations that can maintain the interpretation of these asteroid classes as differentiated objects, with metallic Fe and no FeO present.

### **7.1 OH Creation Through Solar Wind Interaction**

Starukhina (2001) has proposed that solar-wind implanted hydrogen may react with silicates (or other oxygen-bearing minerals) in asteroid regoliths, resulting in OH groups which are detectable spectroscopically but are not indicative of hydrated minerals and which did not originate through aqueous alteration. She calculates that OH created by the solar wind could explain all positive observations of 3- $\mu\text{m}$  absorption bands on asteroids (although she notes that the calculated values for solar-wind-induced band strengths are upper limits and may overestimate the effect). However, this model and these calculations make some predictions which are not borne out: The cal-

culated saturation time for solar wind hydrogen near the equators of main belt asteroids is a few hundred years. Yet, the fraction of asteroids with detectable 3- $\mu\text{m}$  absorption features is far from unity. The calculated band depth for solar-wind-induced OH increases with increasing continuum reflectance, yet no such correspondence is seen in the asteroids. The predicted absorption depth for 4 Vesta is 20% or greater (assuming saturation), but the upper limit on its band depth is 1% (Lebofsky, 1980). As instruments and techniques advance, however, and as observational uncertainties in the 3- $\mu\text{m}$  region will more routinely approach the 1% level, the creation of OH through solar wind interactions will need to be considered in interpreting weak 3- $\mu\text{m}$  absorptions.

## 7.2 Troilite

Cloutis and Burbine (1999) and Fornasier and Lazzarin (2001) suggested that a feature found near 0.5  $\mu\text{m}$  in some E asteroids may be due to troilite (FeS) or other sulfides, and that the mineral responsible may also be responsible for the 3- $\mu\text{m}$  feature in E-class, and perhaps M-class asteroids. If true, this would potentially allow sulfur contents of these asteroids to be determined, and strengthen the interpretation of these bodies as differentiated. Cloutis and Burbine presented spectra of synthetic and natural troilite and pyrrhotite, which showed evidence of a 3- $\mu\text{m}$  absorption feature. However, this feature when seen in troilite is likely due to laboratory contamination by atmospheric water. Because of the high concentration of water in the

Earth's atmosphere and its rapid reaction time with unoxidized material at room temperature, special precautions must be taken in the laboratory to ensure that any absorption features seen are due to the non-terrestrial properties of the sample of interest, particularly in powdered samples. Salisbury *et al.* (1991a) show that adsorbed water either as a result of terrestrial weathering, or simply from exposure of powdered samples to air, can contain up to 2% H<sub>2</sub>O by weight. The 3- $\mu$ m absorption bands shown in Cloutis and Burbine (1999) are similar in depth and shape to those seen on quartz and barite in Salisbury *et al.* (1991b), and attributed to adsorbed water by those authors.

Furthermore, the group of E-class asteroids showing the visible absorption include both those with and without a 3- $\mu$ m feature, and asteroids with the 3- $\mu$ m feature include those both with and without the visible feature (Rivkin and Howell, 2001). Therefore, the two absorptions appear uncorrelated with each other in E-class asteroids.

### **7.3 Is the Observation of Water/OH on Asteroids Meaningful?**

As mentioned above, the strength of the 3- $\mu$ m absorption is such that it can be detected at small concentrations, particularly when it is not mixed with very low-albedo constituents (Clark, 1983). The band strength is enhanced for small particle sizes, which may make a small amount in an asteroid regolith detectable (Salisbury *et al.*, 1991a). Cloutis (2001) argued that

because the 3- $\mu\text{m}$  band is seen in nominally anhydrous materials on the Earth, it is not diagnostic for hydration on the asteroids or Mars when small concentrations are indicated. However, this study used powdered laboratory samples measured in air as a comparison, which is subject to adsorbed water as described above. Cloutis notes that adsorbed water from the Earth's atmosphere may be responsible for the water feature in these nominally anhydrous lab materials. In the hard vacuum of space, with billions of years of temperature cycling, such loosely bound water can be expected to be lost. In addition, in the laboratory, one can measure band depths at 2.8  $\mu\text{m}$ , which for asteroids is a wavelength that is not observable from the ground since telluric water vapor makes the atmosphere opaque. Of necessity, the band depths at 2.95–3.0  $\mu\text{m}$  that are measured on astronomical objects are less than would be seen at 2.8  $\mu\text{m}$  from a spaceborne instrument. In comparing astronomical spectra to laboratory measurements, caution must be used to ensure that the band depth refers to the same spectral region, relative to the same continuum.

## **8 Open Questions and Future Work**

### **8.1 Telescopic work**

The advent of larger telescopes and more sensitive instruments open up a larger number of possible targets for observational work. It is possible now to observe objects with diameters of  $\sim 10$  km or smaller in the main belt and

look for the 0.7- $\mu\text{m}$  band, while 3- $\mu\text{m}$  observations can reach 30 km low-albedo objects. This affords the opportunity to study trends of hydration state with size, following up on the necessarily tentative results presented in Section 6. Near-Earth asteroids also can be studied in greater detail. At the time of this writing, only three NEAs have been observed at 3  $\mu\text{m}$  (433 Eros: Rivkin and Clark, 2001, 4179 Toutatis: Howell *et al.*, 1994a, and 1036 Ganymed: Rivkin, unpublished), all of which are S asteroids, and all of which are anhydrous. The relative paucity of C asteroids in the NEA population has made observing them difficult, but they are sufficiently bright to make them feasible targets for observations at 0.7  $\mu\text{m}$ . Increased instrumental sensitivities and larger telescopes also make it possible to do studies of dynamical/collisional families. This work has been initiated for the 0.7- $\mu\text{m}$  feature, with work by Bus (1999) for the Chloris and Dora families, Florczak *et al.* (1999) for 36 members of the Themis family, and Mothé-Diniz *et al.* (2001) for ten objects in the Hygiea family. Bus found the Chloris and Dora families to both be quite homogeneous in terms of hydration states, while the others found some differences between members of these much larger families. These types of studies should be extended to the 3- $\mu\text{m}$  region. Similarities and differences among band depths and band shapes in a single family would help determine the nature and homogeneity of the aqueous alteration process, and could help determine any dependence upon depth in the parent body.

## 8.2 “Space Weathering” and Impact Processes on Hydrated Asteroids

The effect of regolith processes on determining the olivine and pyroxene abundances on an airless surface is an area of much current research. These “space weathering” effects are described in detail in the chapter by Clark et al. We note that these studies are of great importance to studies of hydrated minerals. If the spectral effects are greater at visible wavelengths than in the infrared, as it appears currently, the relative strengths of the 0.7 and 3- $\mu\text{m}$  features may be usable as a maturity metric for hydrated asteroids. If these processes can cause diminished band depths for the hydration bands, attempts to accurately determine water contents will be complicated, but lower limits can still be found.

The effect of large impacts on the volatile budget of asteroids is still unknown. Impacts may dehydrate hydrated target material, although inefficient energy coupling may leave most of the ejecta largely unaffected. Furthermore, the most-heated fraction of ejecta may also be the fraction least likely to be retained on an asteroid. The presence of phyllosilicates in interplanetary dust particles (IDPs) (Rietmeijer and MacKinnon, 1985; Zolensky and Keller, 1991; Keller and Zolensky, 1991) suggests that hydrated minerals can survive not only impact and ejection but millions of years in vacuum, followed by atmospheric entry. Experiments designed to study the spectral changes in phyllosilicates due to impacts have been attempted. Boslough

*et al.* (1980) took spectra of shocked and unshocked nontronite and serpentine, and found that the absorption features due to OH and H<sub>2</sub>O decreased after shocking. However, the post-shock features were still quite strong, and the shock technique was not truly analogous to an impact. Thibault *et al.* (1997) performed impact experiments on serpentine and obtained reflectance spectra of serpentine pre- and post-impact, finding that the 1.9- $\mu\text{m}$  H<sub>2</sub>O feature was gone, but the 1.4- $\mu\text{m}$  OH feature (and presumably the 2.7- $\mu\text{m}$  fundamental) was largely unchanged. Obviously, hydrated minerals can survive family-forming impacts on an asteroid-wide scale, as shown by the prevalence of Ch and Cgh asteroids (which have the 0.7- $\mu\text{m}$  feature) in the Dora and Chloris family (Bus, 1999).

As better data and analysis help determine the identities and relative abundances of specific hydrated minerals present on asteroidal surfaces, and we begin to understand how the surface constituents reflect internal compositions, aqueous alteration models will necessarily benefit. At this writing, these models have focused almost entirely on the meteorite record, without benefit of much in the way of asteroidal constraints. Future telescopic work will sample a much larger range of parent bodies and further limit the formation conditions of hydrated minerals.

## 9 The Big Picture, in Water Colors

The presence of 3- $\mu\text{m}$  and 0.7- $\mu\text{m}$  absorption features on some (but not all) asteroids tells us that hydrated minerals can persist on the surface of airless bodies, presumably since early in solar system history. Whatever regolith maturation may be occurring on 1 Ceres, 2 Pallas, 13 Egeria, and other large asteroids does not destroy the signature of the hydrated minerals present. The first-order correlation of this feature with taxonomic classes is similarly important. If it were found on all asteroids, in all classes, it would suggest an exogenic process (like micrometeorite impacts) brought in the hydrated minerals. However, because the S asteroids as a group are very unlikely to have hydrated minerals compared to the C-class asteroids, we can infer that the hydrated mineralogy of the asteroid classes is an intrinsic compositional difference. The same is true even at sub-class levels, where nearly every one of the G-class asteroids has a 3- $\mu\text{m}$  absorption feature, while only one of the F-class asteroids does despite the same sample size for each class. The large-scale generation of OH by solar-wind generated reactions on all these asteroids can be rejected by the same reasoning, as detailed in Section 7.

The depth of the 3- $\mu\text{m}$  absorption feature also makes any exogenic origin unlikely. Take, for example the hydrated M-class (W-class) asteroids, which have band depths on the order of 5-10%. This is in contrast to asteroids like 16 Psyche, 45 Eugenia, and 185 Eunike, which all have upper limits of 1-2% for 3- $\mu\text{m}$  band depth. If the feature on the hydrated Ms were due to

carbonaceous micrometeorites, these micrometeorites would need to comprise at least several percent of the regolith to give an absorption feature of this depth, assuming a 100% band strength for the carbonaceous micrometeorites. Yet these micrometeorites would have had to avoid the asteroids which show no feature.

In summary, we conclude the following:

1. Almost every taxon has both hydrated and anhydrous members based on their 3- $\mu\text{m}$  spectra. For some taxa (*e.g.* Ms), this probably is the result of disparate mineralogies having similar spectra in the 0.3–2.5  $\mu\text{m}$  region. For others (*e.g.* Cs), both hydrated and anhydrous versions of the same mineralogy are probably present. The fraction of hydrated members is different in the different classes, ranging from  $\sim 65\%$  for the C class to  $\sim 5\%$  for the S class.
2. Broadly speaking, there appear to be two kinds of 3- $\mu\text{m}$  band shapes. A “checkmark” shape is much more common in our sample among low-albedo asteroids than a rounded shape. A rounded shape is more common among the higher-albedo hydrated asteroids. Ceres has a modified rounded shape, as does 375 Ursula, implying that the hydrated mineral assemblage on Ceres may be rare but is not unique.
3. The presence of a 0.7- $\mu\text{m}$  feature appears to be sufficient to identify the presence of hydrated minerals. The lack of such a feature does

*not* appear to be sufficient to rule out the presence of hydrated minerals (since the 3- $\mu\text{m}$  feature is more sensitive, and some higher-albedo asteroids do not appear to have 0.7- $\mu\text{m}$  features).

4. Used in tandem, the 0.7- and 3- $\mu\text{m}$  absorption features may constrain the maximum heating a body has experienced, though that heating may have been strongly non-uniform.
5. Rotational variation is common if not ubiquitous in larger-diameter asteroids, but it is uncertain if this is a remnant of formation or the result of thermal or impact evolution. Rotational variation also appears to explain past discrepancies between low-albedo asteroid hydration states as determined from 0.7- and 3- $\mu\text{m}$  observations.

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## 10 Figures

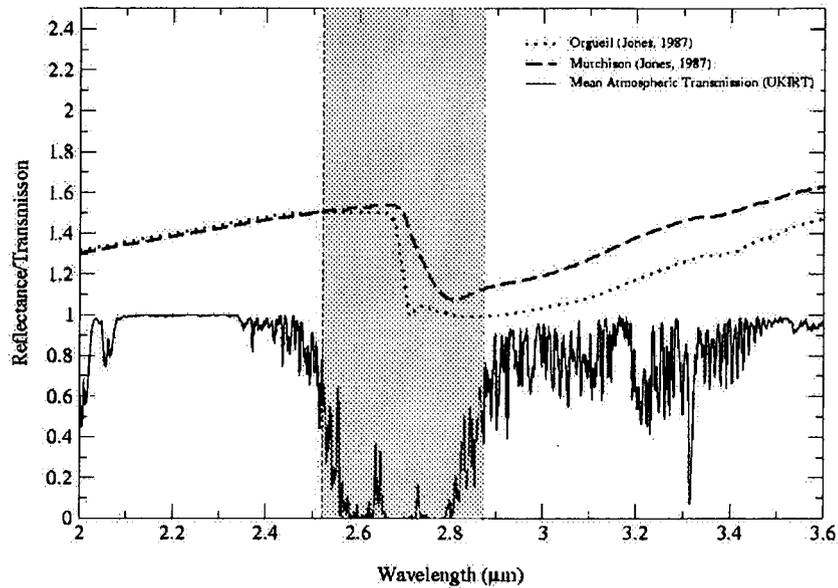


Figure 1: A comparison of atmospheric transmission and laboratory meteorite spectra: Although the 2.52–2.85  $\mu\text{m}$  region has less than 50% transmission, and the 2.56–2.82  $\mu\text{m}$  region less than 10%, the meteorite absorption features are sufficiently wide that they are easily detectable in areas of greater transmission. The shaded area has less than 50% transmission. The meteorite spectra, from Jones (1987), have been offset by 0.5 units for clarity. The atmospheric data are from the UKIRT web site using the program IRTRANS4, assuming an altitude of 4200 m, an airmass of 1.0, and 1.2 mm precipitable water.

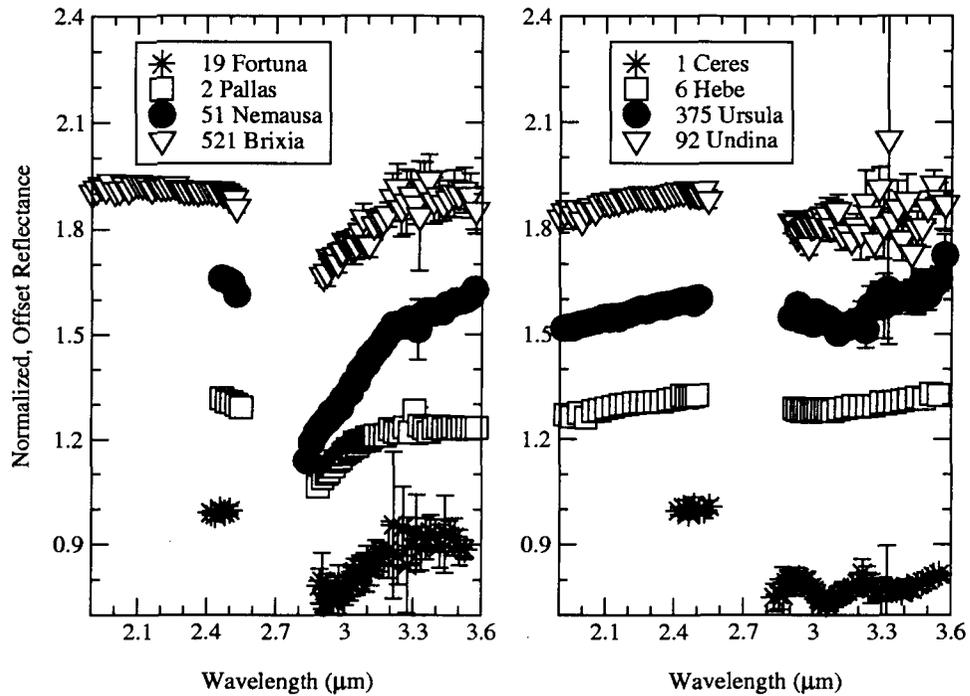


Figure 2: “Checkmark” vs. “round” shaped features. The asteroids on the left all exhibit “checkmark”-shaped absorption features at 3  $\mu\text{m}$ : their reflectance rises monotonically in a nearly linear fashion. Those on the right have a more rounded feature. Most C-class asteroids with 3- $\mu\text{m}$  absorptions tend to have the check-shaped feature. Higher-albedo objects with features have rounded ones, though shallow band depths make this difficult to determine at times. Ceres and Ursula are notable exceptions to this rule of thumb. Rounded features are reminiscent of  $\text{H}_2\text{O}$ -dominated minerals, while the checkmark shapes are more similar to OH-dominated ones. Thermal corrections have been applied to these data using the Standard Thermal Model. These data were obtained by A. Rivkin and J. Davies at UKIRT, and the manuscript is in preparation. Error bars are included in this graph, although for most of the spectral region they are smaller than the points.

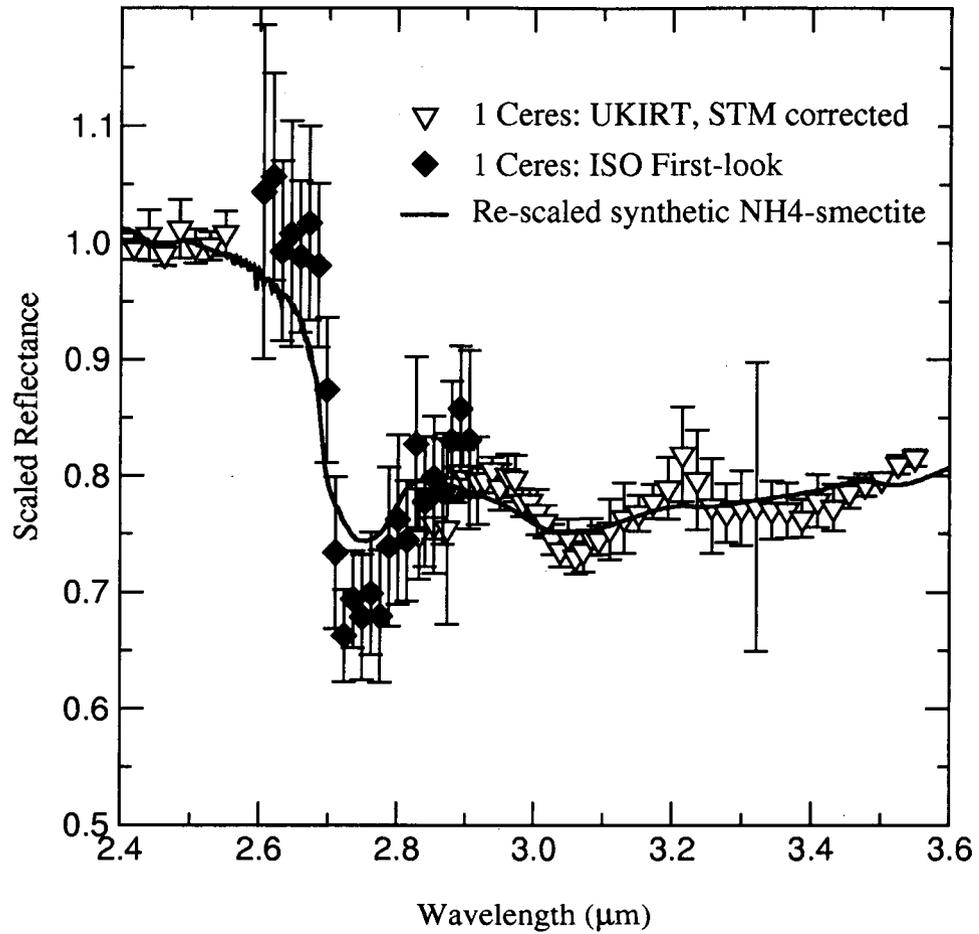


Figure 3: First-look ISO data for Ceres, plus CGS4 UKIRT data (both from Rivkin (1997), vs. ammoniated smectite from T. King (pers. comm.) The smectite spectrum has been mathematically mixed with a spectrally neutral material to match Ceres' band depth. The match is quite good, including in the region visible only from space.

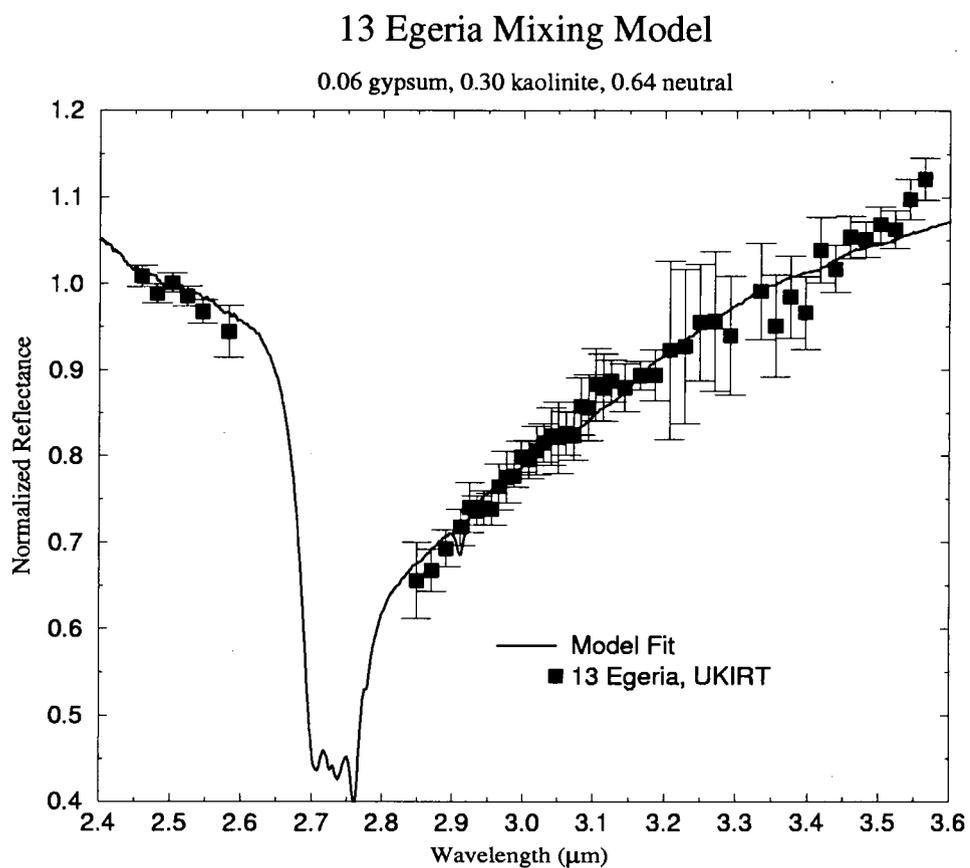


Figure 4: Fit to 13 Egeria using minerals from the Salisbury et al. (1991) spectral library. A non-linear mixing code using the Hapke equations was used in this fit (Clark et al. 1993; Clark et al. in press). Figure taken from Rivkin (1997)

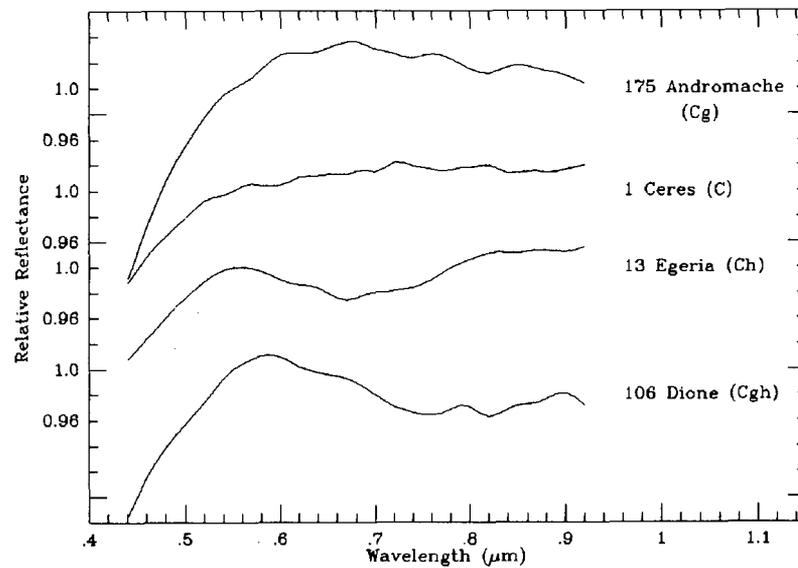


Figure 5: The spectra shown are taken as part of the SMASS II survey (Bus 1999). The Tholen C and G classes are re-organized primarily into the C, Cg, Ch and Cgh classes. The 'g' is appended to those objects whose spectra turn down sharply at the 0.44  $\mu\text{m}$  end. The 'h' is appended to those objects whose spectra show the broad iron charge-transfer feature near 0.7  $\mu\text{m}$ . Some objects have both of these features. The iron features near 0.43  $\mu\text{m}$  and 0.65  $\mu\text{m}$  are narrower, and do not show clearly at this scale.

## Murchison: spectral changes with heating

From Hiroi et al. (1996)

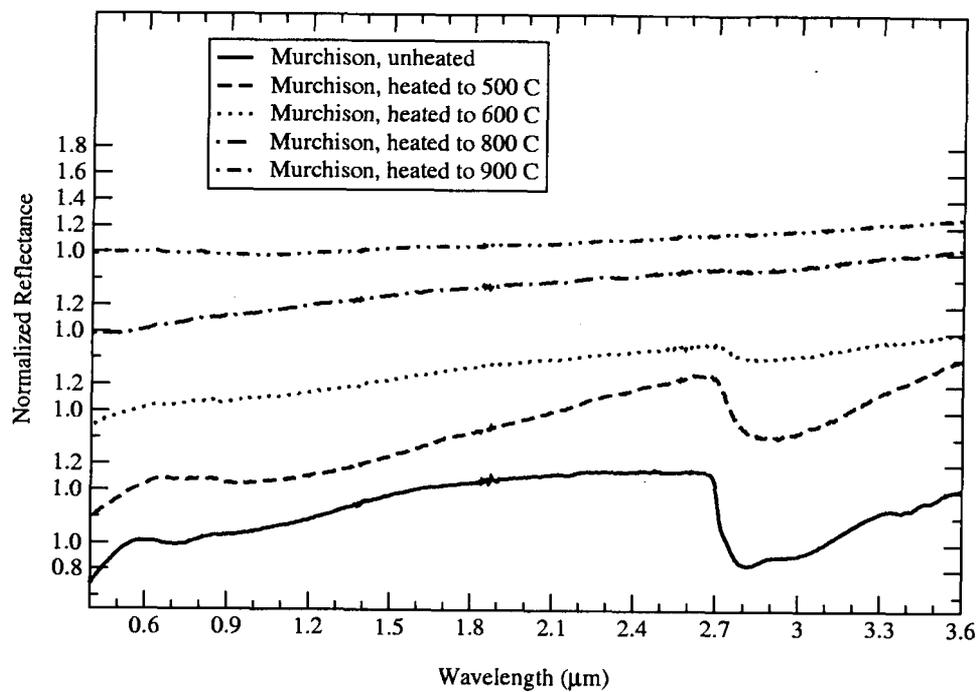


Figure 6: Spectra of the CM Murchison, taken after heating to different temperatures. Mild heating drives off adsorbed water, but leaves the structural water and OH. Further heating dehydrates and destroys the matrix phyllosilicates, with the 3- $\mu\text{m}$  band disappearing as a result.

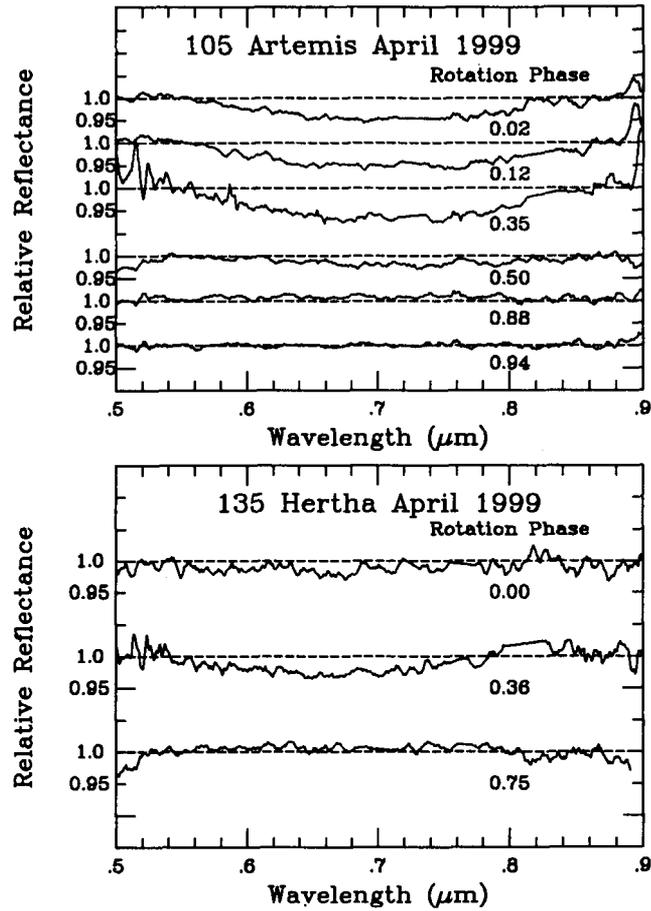


Figure 7: Visible spectra were obtained at different rotational phases using the 2.1-m telescope at McDonald Observatory. The spectra show changes in the absorption band at  $0.7\mu\text{m}$  as the asteroid rotates. The upper plot shows that 105 Artemis has an absorption feature on one hemisphere, but not on the other. The lower plot shows a feature at one rotation phase of 135 Hertha. These variations are interpreted as localized areas of hydrated silicates exposed on the surface. This inhomogeneity could be in the regolith, or the underlying material, or both.

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